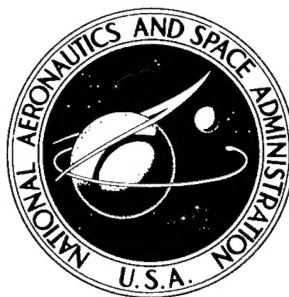


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# THE ERECTED DIPOLE MODEL IN THE ADSORPTION OF CESIUM ON FLUORINATED MOLYBDENUM

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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SUMMARY

[Interest in power-producing thermionic diodes containing both electropositive and electronegative additives has lead to studies of the structure of adsorbed layers. One of the models advanced to describe this layer is that of the erected dipole, in which polar molecules are erected on a surface by a strong surface electric field. Published evidence for this structure in the case of some adsorbates, namely, barium oxide and cesium chloride, is reviewed.

A modified version of the erected dipole model, presented in this report, was used to analyze published data for the system cesium on fluorinated molybdenum. The results are compared with data in the literature and suggest that cesium fluoride molecules are adsorbed as erected dipoles in this system. The effect of this configuration on work function for the system cesium on fluorinated molybdenum as temperature is raised is discussed. Also discussed is the strength of the electric field associated with the surface, which is responsible for the erection of the dipoles.]

INTRODUCTION

The advantages of additives in power-producing thermionic diodes have been known for some time. Materials such as cesium (ref. 1), barium (refs. 2 and 3), and strontium (ref. 2) can be of benefit either because of their electrical effect on the solid surfaces or upon the plasma between the surfaces, or both. Cesium, for instance, lowers the work function of metallic surfaces upon which it is adsorbed, increasing electrical current. Because it forms positive ions readily, it can also help to neutralize the negative space charge of the electrons between the surfaces.

It is also known that favorable effects can be obtained in thermionic devices by the simultaneous presence of both metallic and nonmetallic additives. In such a composite system, both species are adsorbed together on the surface. Under desirable conditions the work function is lowered considerably, as it is in the case of the metallic additive alone. In addition, the multiple coating may desorb less readily, extending to higher temperatures the beneficial effect

of additives on work function.

Among the multiple coatings that have been studied are alkaline earth oxides on metal filaments (Moore and Allison, ref. 4; and Gavriliuk, ref. 3) and on field emission microscope tips (Noga, ref. 5). Filaments coated with cesium chloride were investigated by Morgulis and Gavriliuk (ref. 6).

Of late, systems containing cesium and fluorine have received much attention. Aamodt, et al. (ref. 7) and Ranken, et al. (ref. 8) studied the thermionic emission of a metal filament first coated with fluorine and then exposed to cesium. A thermionic diode containing vapors of both cesium and cesium fluoride was studied by Skeen (refs. 9 and 10).

A thorough understanding of composite or multiple additive systems requires that the structure of the surface layer be elucidated. At least two structures have been proposed for such systems. In one, the nonmetallic atoms and the metallic atoms are considered to be adsorbed side by side on separate sites (Carabateas, ref. 11). In the other, advanced at various times by several authors (Moore and Allison, ref. 4; Morgulis and Gavriliuk, ref. 6; and Dykman, ref. 12), adsorption of the two species as diatomic molecules is postulated. It is proposed that these molecules, having some permanent electric dipole moment, are erected on the surface with the positive end outward. The resulting electric double layer is presumably responsible for the observed decrease in work function.

In the present report the data of Aamodt, et al. (ref. 7) are analyzed in some detail in an attempt to clarify the structure of the composite coating for the cesium-fluorine system. A mathematical model of cesium fluoride molecules erected on the surface by a strong surface electric field was used. The theory of Dykman (ref. 12) was modified to match the experimental conditions under which the data of Aamodt, et al. were obtained. The computed strength of this electric field is compared to those calculated from other experimental data by investigators whose studies support the erected dipole concept. Further comparisons are made with electric field strengths reported for monatomic adsorbates, which cannot be erected. Additional calculations of surface electric field were made from published data for monatomic adsorbates and are reported herein.

## DISCUSSION AND RESULTS

### Evidence for the Erection of Some Adsorbed Molecules

Prior to the analysis of data for cesium on fluorinated molybdenum, the subject of this report, evidence from several sources for the adsorption of some molecules as erected electric dipoles will be reviewed. Parameters such as surface electric field and electric dipole moment of the erected molecules, reported in these papers, will be discussed.

Adsorption of barium oxide and cesium chloride on tungsten. - Moore and Allison (ref. 4) seem to have been the first to advance the concept of the erected adsorption of barium oxide molecules, as illustrated in figure 1.

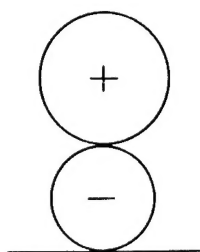


Figure 1. - Erected adsorption of polar molecule.

For the low-coverage adsorption of barium oxide on tungsten, they observed that work function changed at the rate of -40 electron volts per monolayer. This rate persisted for only a very small fraction of a monolayer. From this information, an electric dipole moment for the adsorbed barium oxide (BaO) molecule can be computed as follows: The equation for work function difference upon adsorption (ref. 13, pp. 52 and 53)

$$\Delta\phi = \phi - \phi_0 = -4\pi\sigma p_n \quad (1)$$

is differentiated with respect to coverage, treating  $p_n$  as constant, to give

$$\frac{d\Delta\phi}{d\sigma} = -4\pi p_n \quad (2)$$

where

$\Delta\phi$  work function difference, stat V (1 stat V = 299.8 V)

$\phi$  work function, stat V

$\phi_0$  work function of bare surface, stat V

$p_n$  component of dipole moment of adsorbed molecule normal to surface, (stat C)(cm)

$\sigma$  adsorbed dipole density, particles/sq cm

(Symbols are also defined in appendix A.)

The definition of a monolayer in reference 4 was based on a nearest neighbor distance of 2.75 angstroms which gives  $1.33 \times 10^{15}$  molecules per square centimeter in a square lattice. For the present report, this value, together with the aforementioned rate of change of work function with coverage, was inserted in equation (2). The value of  $p_n$  obtained thereby for a condition of low coverage turns out to be 8.0 debye (1 D =  $10^{-18}$  (stat C)(cm)).

Wharton, et al. (ref. 14) measured a dipole moment of 7.955 debye for the ground state of a gaseous barium-oxide molecule. These authors state that this corresponds to a singly ionic polar molecule (one electron transferred from the barium to the oxygen atom). The data of Moore and Allison thus suggest that the adsorbed BaO molecule can be viewed as erected and singly ionic.

Noga (ref. 5) studied the adsorption of BaO on the tungsten emitter tips of a field-emission microscope. From a measured  $d\phi/d\sigma$  of -25 volts per monolayer he computed a  $p_n$  of  $13.5 \pm 8$  debye using the same definition of a monolayer as Moore and Allison. The calculation seems to be in error.

Gavriliuk (ref. 3) studied the adsorption of BaO on tungsten filaments. Inserting the measured rate of change of work function at low coverage in

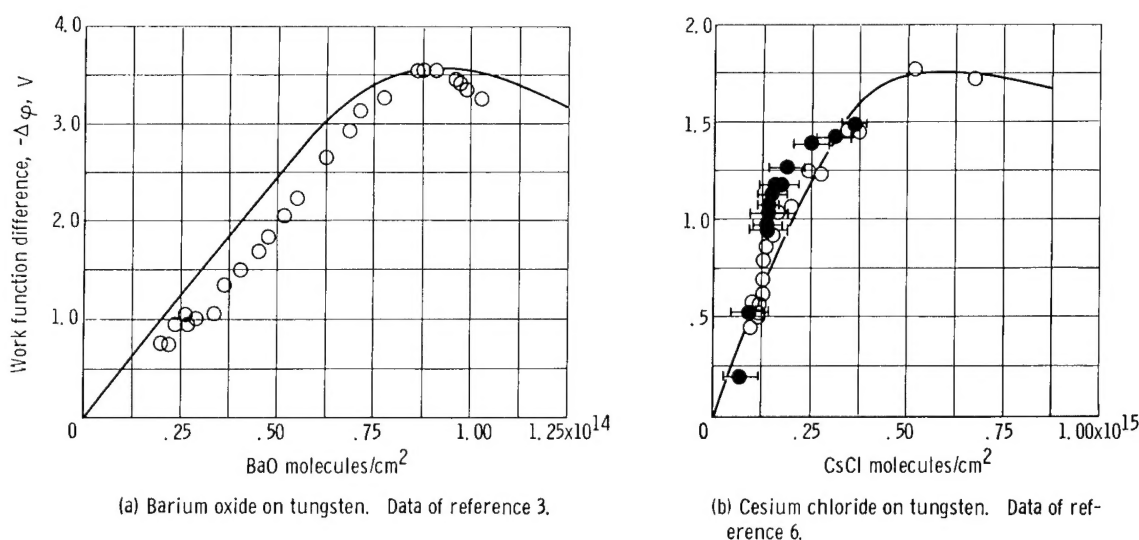


Figure 2. - Work function difference in adsorption of molecular species on tungsten filaments as function of surface concentration. Figure replotted from reference 12.

equation (2), he found a value of 9.4 debye for the electric dipole moment of the BaO molecule.

Morgulis and Gavriluk (ref. 6) observed the adsorption of cesium chloride on tungsten filaments. In the latter paper the concept of the erected dipole was offered to explain observations in the adsorption of BaO and cesium chloride (CsCl). Figure 2 herein represents some of the data of references 3 and 6 as plotted by Dykman (ref. 12). Work function difference against adsorbate coverage is shown for BaO and for CsCl.

In both cases a clearly defined maximum in  $-\Delta\phi$  is observed, implying a minimum in  $\phi$ . A minimum in  $\phi$  is also observable in some of the BaO data of Noga (ref. 5). In the case of the barium oxide data of Moore and Allison (ref. 4) it is not seen. There is a possibility that their data points were not spaced closely enough to delineate a minimum.

Analysis of barium oxide and cesium chloride data by Dykman. - Dykman, observing the minima in the data of references 3 and 6 as shown in figure 1 herein, offered an explanation in terms of erected but oscillating dipoles. He regarded the dipoles as having available to them any angle  $\theta$  with respect to the surface normal from zero to  $\pi$  radians, as suggested by figure 3. He postulated the existence of a permanent electric field  $\vec{E}_0$ , associated with the

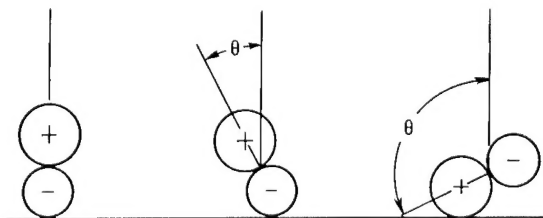


Figure 3. - Erected adsorption of polar molecule with oscillation.

surface, which was responsible for giving the molecules a mean orientation with the positive ion outward. Dipoles with their positive ends away from the surface give rise to an electric field which decreases the permanent erecting field  $\vec{E}_0$  as coverage increases. As a consequence, the mean value of  $\cos \theta$  decreases with coverage. For this model,

$$p_n = p \overline{\cos \theta} \quad (3)$$

so that the work function difference is given by

$$\Delta\phi = -4\pi p \sigma \overline{\cos \theta} \quad (4)$$

where

$p$  magnitude of moment of adsorbed dipole (taken constant)

$\overline{\cos \theta}$  mean value of  $\cos \theta$

While  $\sigma$  increases, the decrease in  $\overline{\cos \theta}$  causes  $-\Delta\phi$  to pass through the maximum observed in figure 2.

Dykman evaluated  $p$  and  $\vec{E}_0$  for the adsorption of BaO and CsCl on tungsten by means of figure 2, in the following manner. He showed that  $\overline{\cos \theta}$  was given by

$$\overline{\cos \theta} = L(\eta) \quad (5)$$

where

$$L(\eta) = \coth \eta - \frac{1}{\eta} \quad (6)$$

which is the Langevin function and

$$\eta = \frac{pE}{kT} \quad (7)$$

where

$E$  magnitude of surface electric field (in this case also normal component), stat V/cm

$k$  Boltzmann constant, ergs/ $^{\circ}$ K

$T$  temperature of surface,  $^{\circ}$ K

A derivation paralleling Dykman's, but for two adsorbed species, is given in appendix B. Dykman's equations are obtainable from the derivation.

Equations (5) to (7) describe a situation analogous to that of rigid polar gaseous molecules in an electric field (ref. 15). In the case of adsorption there is a complication. The erected dipole produces a field which opposes  $E_{0n}$ , the normal component of  $\vec{E}_0$ . Because of the very high surface densities the field of the dipoles appreciably weakens the surface electric field. Dykman showed that the net field acting on the dipole could be expressed as

$$E = E_0 - \beta \sigma^{3/2} p \overline{\cos \theta} \quad (8)$$

where the Topping constant  $\beta \approx 9$  (appendix B).

The mean tangential field is zero making  $E_0$ , the magnitude of  $\vec{E}_0$ , equal to  $E_{0n}$ .

Dykman solved equation (4), together with its first derivative

$$\left[ \frac{\partial(-\Delta\phi)}{\partial \ln \sigma} \right]_T = 4\pi\sigma p L(\eta) \left[ 1 + \left( \frac{\partial \ln L}{\partial \ln \sigma} \right)_T \right] \quad (9)$$

for  $E_0$  and  $p$ , by inserting in them the conditions at the maxima of figure 2. For BaO on tungsten (W) these conditions are that

$$\left[ \frac{\partial(-\Delta\phi)}{\partial \ln \sigma} \right]_T = 0$$

and  $-\Delta\phi \approx 3.5$  volts when  $\sigma = 0.9 \times 10^{14}$  molecules per square centimeter. An iteration is required in solving equations (4) and (9) simultaneously. The results are listed in table I.

The dipole moment of 14 debye for BaO in table I is somewhat higher than the value of 9.4 debye computed by Gavriluk (ref. 3) from the same data at the low coverage condition ( $\sigma \rightarrow 0$ , eq. (2)). The data of Moore and Allison give a value of 8.0 debye at low coverage, while Wharton, et al. report 7.955 debye for BaO gas molecules, as mentioned earlier.

On the other hand, the value of 1.74 debye for adsorbed CsCl is quite different from the experimental value of 10.42 debye determined by Trischka (ref. 16) for gaseous CsCl. A possible explanation of this difference is that a portion of the CsCl molecules was not erected upon the surface. After deposition of CsCl, Morgulis and Gavriluk heated their filaments to 600° C for 1 minute. If the dipoles after deposition were adsorbed horizontally on the surface, it is possible that this heat treatment was insufficient to erect all of them. Noga (ref. 5) comments that the erection of BaO dipoles on his field emitter tips seemed more satisfactory at higher temperatures than at room temperature.

An alternate explanation of the low value of  $p$  calculated for CsCl is that some of the cesium may have been driven off by heating, leaving a portion

TABLE I. - PARAMETERS IN ERECTED DIPOLE ADSORPTION MODEL

FOR BARIUM OXIDE AND CESIUM CHLORIDE ON TUNGSTEN

[Computed in ref. 12 from data in refs. 3 and 6.]

Adsorbate	Electric dipole moment, $p$ , debye	Permanent surface electric field, $E_0$	
		stat V/cm	V/cm
Barium oxide	14	$1 \times 10^5$	$3 \times 10^7$
Cesium chloride	1.74	1.33	4



of the surface covered by chlorine alone. As indicated by the studies of Silver and Witte (ref. 17), chlorine adsorbed alone increases the work function. The presence of some uncombined chlorine atoms would thus require an adjustment to equation (1).

#### Erected Adsorption of Cesium Fluoride on Molybdenum

Further evidence concerning the model of the erected dipole in the adsorption of diatomic molecules comes from data of Aamodt, et al. (ref. 7) for cesium on fluorinated molybdenum. The equations of Dykman were modified to enable these data to be analyzed in the light of the erected dipole model. Aamodt, et al. described experiments in which a cesium atmosphere contacted hot molybdenum filaments, either bare or coated previously with fluorine. They presented figures showing curves of electron emission current against temperature at various cesium reservoir temperatures for both the plain and the fluorinated filaments. The curves for cesium on fluorinated molybdenum (Mo) have been reproduced as figure 4 herein. The data in figure 4 represent a quasi-steady-state condition.

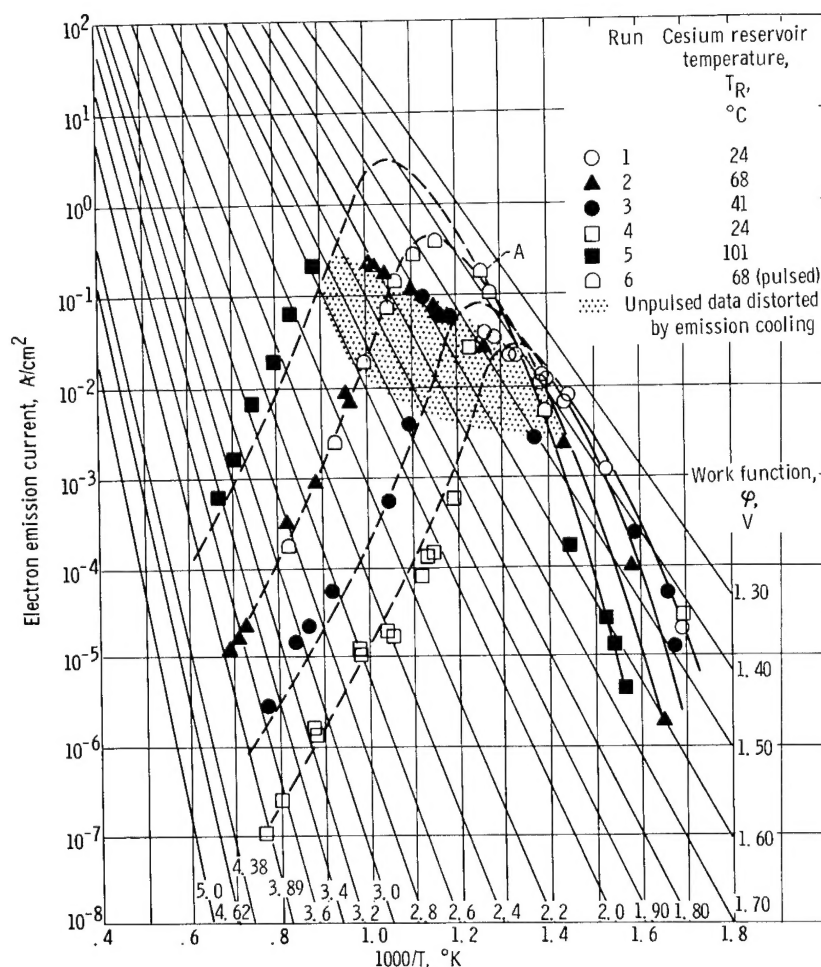


Figure 4. - Electron emission from fluorine-coated Mo in Cs atmosphere. (Data of ref. 7.)

Cesium atoms arrive at, and depart from, the surface in equal numbers so as to maintain a constant coverage of cesium at any condition. While the fluorine atoms are not replenished, the rate of desorption of fluorine may safely be presumed to be many orders of magnitude less than that of the cesium. Aamodt, et al. present data for the fluorine coating alone showing only about 15 percent change in work function of the fluorine coating at 1683° K over a period of 5 hours. Very little of the data in figure 4 were taken at temperatures exceeding this. For the data in figure 4, the coverage of fluorine atoms may thus be expected to remain virtually unchanged during a given run. Exceptions, as noted by the authors, exist where back-bombardment of the filament by cesium ions from the collector caused some fluorine coating to be removed during preliminary adjustment.

Referring to figure 4, it is seen that as  $1/T$  is increased at constant cesium reservoir temperature (constant arrival rate), the work function definitely falls to a minimum and then rises. Run 6, showing this effect clearly, was the run from which the data were taken for the analysis reported herein. A minimum work function of about 1.36 electron volts, designated as point A, was attained at a temperature of about 800° K, with a cesium reservoir temperature of 68° C. The corresponding plot for cesium on unfluorinated molybdenum (not reproduced here) shows a far smaller rise in work function as  $1/T$  is increased beyond the point of minimum work function.

As temperature falls ( $1/T$  increasing) in run 6 of figure 4, the amount of cesium increases on the surface. Beyond the minimum work function, additional cesium results in an increase in work function. This is suggestive of the effect observed for the systems BaO and CsCl on tungsten (refs. 3 and 6) as shown in figure 2 (p. 4). It will be recalled that for these systems it was postulated that the increasing concentration of dipoles on the surface weakened the surface electric field, resulting ultimately in a minimum in work function.

The data of figure 4 for CsF on molybdenum will be analyzed in the light of the erected dipole model by supposing that the adsorbed cesium atoms during their stay on the surface are paired with fluorine atoms to form erected dipoles. Furthermore, it will be supposed that upon desorption of the cesium, the fluorine atoms remain behind. A value for the electric field  $E_0$  and the coverage at minimum work function can be computed by modifying the theory of Dykman (ref. 12) to account for the uncombined fluorine and for the variation of filament or emitter temperature during a run.

It will be recalled that Dykman knew, for the data he analyzed, dipole coverage against work function. From these he computed  $E_0$  and moment  $p$  of the erected dipole. If, instead, a value for the dipole moment  $p$  is assumed without the coverage being known, the coverage at the point of minimum work function and the field  $E_0$  can be computed.

In order to make such a computation the equations of Dykman (ref. 12) must be altered to account for those adsorbed fluorine atoms which are uncombined with cesium. In the studies (refs. 3 and 6) from which Dykman drew his data, the CsCl and BaO were vaporized from a source filament onto the emission filament. Dykman, therefore, could assume that only the diatomic additive was

present. In the experiments of Aamodt, et al. (ref. 7), the excess fluorine atoms themselves formed dipoles, possibly by the partial extraction of electrons from the metal surface. An indication of the strength of these dipoles is given by the work function difference of 0.6 volt observed for fluorine alone on molybdenum (fig. 9 of ref. 7). It will be supposed that these dipoles contributed to the surface electric field.

The details of an analysis of the data in figure 4 are given in appendix C. In brief, equation (4) is replaced by

$$\Delta\phi = -4\pi\sigma_1 p_1 \overline{\cos \theta} - 4\pi\sigma_3 p_3 \quad (10)$$

(see eq. (C1)) where

- $\sigma_1$  number of adsorbed CsF molecules/cm<sup>2</sup>
- $\sigma_3$  number of adsorbed F atoms/cm<sup>2</sup> (not combined with cesium)
- $p_1$  magnitude of electric dipole moment of adsorbed CsF molecule (taken constant), (stat C)(cm)
- $p_3$  magnitude of electric dipole moment of adsorbed F atom (taken constant), (stat C)(cm)

The fluorine dipoles are regarded as being always normal to the surface. Subscript 2 has been reserved for possible future use. Equation (8) is replaced by

$$E = E_0 - \beta\sigma_1^{3/2} p_1 \overline{\cos \theta} - \beta\sigma_3^{3/2} p_3 \quad (11)$$

(see eq. (B9)), and equation (9) is replaced by

$$\frac{\partial(-\Delta\phi)}{\partial \ln \sigma_1} = 4\pi\sigma_1 p_1 L \left[ 1 + \left( \frac{\partial \ln L}{\partial \ln \sigma_1} \right)_T + \left( \frac{\partial \ln L}{\partial \frac{1}{T}} \right)_{\sigma_1} \left( \frac{\partial \frac{1}{T}}{\partial \ln \sigma_1} \right)_{T_R} - \frac{p_3}{p_1 L} \right] \quad (12)$$

(see eq. (C11)) where

- $T_R$  cesium reservoir temperature
- $T$  filament or emitter temperature

As in equation (C5),  $\sigma_3$  is here regarded as a function of  $\sigma_1$ .

Equation (12) differs from equation (9) in the presence of the derivative product

$$\left( \frac{\partial \ln L}{\partial \frac{1}{T}} \right)_{\sigma_1} \left( \frac{\partial \frac{1}{T}}{\partial \ln \sigma_1} \right)_{T_R}$$

and the term  $p_3/p_1 L$ . These terms can be shown to be small compared to unity, with the latter term larger. The present case for the Cs-F-Mo system thus resembles closely that of BaO and CsCl on W (ref. 12). Equations (5) to (7) retain their form for the present case (see appendix B).

Equations (10) and (12) were evaluated for  $E_0$  and  $\sigma_1$  at the conditions of point A, figure 4 (work function, 1.36 V; filament temperature, 800° K). In making the computation, it was assumed that the dipole moment of an adsorbed CsF atom is the same as a gaseous atom, reported as 7.875 debye by Trischka (ref. 16). Such an assumption neglects the polarization of the molecule in the surface electric field.

The electric field  $E_0$  of molybdenum was computed to be about  $3.54 \times 10^7$  volts per centimeter ( $1.18 \times 10^5$  stat V/cm), with corresponding CsF coverage  $\sigma_1$  about  $2.0 \times 10^{14}$  molecules per square centimeter. The value of  $E_0$  is quite comparable to those computed by Dykman (ref. 12) from the adsorption of BaO and CsCl on tungsten (table I, p. 6), although they are for another substrate.

Effect of the erected dipole configuration on work function. - As temperature is increased at constant coverage,  $\cos \theta$  can be shown to decrease. As a consequence, work function must increase, by equations (4) or (10). This effect will be illustrated for the cesium-fluorine system.

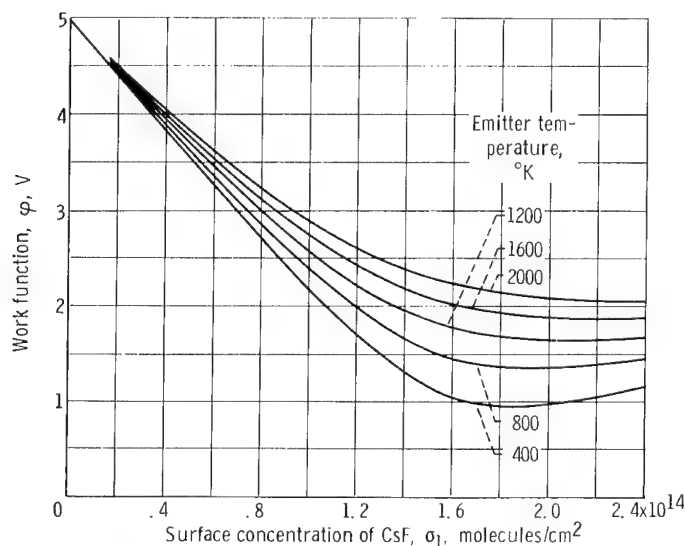


Figure 5. - Work function of cesium on fluorinated molybdenum against surface concentration of cesium fluoride molecules for various emitter temperatures.

The work function of cesium on fluorinated molybdenum was computed by means of equation (10) using a  $p_1$  of 7.875 debye and an electric field  $E_0$  of  $3.54 \times 10^7$  volts per centimeter as described in the previous section. Figure 5 shows  $\phi$  against  $\sigma_1$  for a series of emitter temperatures. It is seen that the minimum work function attainable at any emitter temperature rises with the emitter temperature. It must be recalled, however, that the multiple coating persists to higher temperature than possible with cesium on molybdenum alone, making a net gain in performance possible.

## Other Evaluations of Surface Electric Field Strength

Adsorption of rare gases on tungsten. - The foregoing value of  $E_0$  computed from Cs adsorption on fluorinated Mo, and those in table I for BaO and CsCl on W are of interest since they can be compared with values from other sources. A surface electric field strength  $E_0$  can be computed from observations of inert gas adsorption on tungsten. Ehrlich and Hudda (ref. 18) studied the adsorption of rare gases on tungsten with a field emission microscope. They, too, advanced the concept of a surface electric field in interpreting their results, and computed its value from one data point. For xenon at 85° K they found a  $-\Delta\phi$  of 0.7 volt for an assumed coverage of  $2 \times 10^{14}$  atoms per square centimeter (partial coverage). From this data, a dipole moment of 0.93 debye and a field of  $6.9 \times 10^7$  volts per centimeter were computed.

Ehrlich and Hudda present additional data for argon (Ar), krypton (Kr), and xenon (Xe) from which other values of  $E_0$  can be computed. Table II summarizes the portion of the information contained in table I of reference 18 needed for such calculations.

It seems reasonable here to assume that the data taken at 20° K represents approximately monolayer coverage, as suggested by the Xe data. Most of the decline in work function occurred between 85° and 79° K. The further small change when the temperature was dropped to 20° K appears to have assured monolayer saturation. On the other hand, in the case of Ar, excessive pressure at 20° K caused a rise in  $\phi$ , probably due to multilayer adsorption. The  $\phi$  values of 3.00 and 3.63 volts, taken as representative of monolayer coverage for Xe and Ar, respectively, agree well with numbers found by Gomer (ref. 19).

The density of atoms in a monolayer  $\sigma_m$  can be computed by assuming hexagonal closest packing and is shown in table III. This has been a frequent assumption in the estimation of surface areas by gas adsorption (Young and Crowell, ref. 20, p. 226 et seq.). The distance  $r_0$  of the nearest neighbor in closest

TABLE II. - WORK FUNCTION CHANGES ON ADSORPTION OF  
XENON, KRYPTON, AND ARGON ON TUNGSTEN

[Data from ref. 18.]

Adsorbate	Polarizability, $\alpha$ , cm <sup>3</sup>	Distance of nearest neighbor (close packing), $r_0$ , Å	Emitter temperature, °K	Gas pressure, mm Hg	Work function, $\phi$ , V
Xenon	$40.1 \times 10^{-25}$	4.41	85 79 20	$5 \times 10^{-9}$ ↓	3.78 3.12 3.00
Krypton	24.8	3.95	20	$10^{-10}$	3.32
Argon	16.3	3.84	20 20	$< 10^{-10}$ $>> 10^{-10}$	3.63 4.10

TABLE III. - PARAMETERS IN POLARIZED ADSORPTION OF  
SOME RARE GASES ON TUNGSTEN

[Computed from data in table II.]

Adsorbate	Monolayer density, $\sigma_m$ , atoms/cm <sup>2</sup>	Maximum $-\Delta\phi$ , V	Permanent surface electric field, $E_0$ , V/cm	
			With mutual interaction	Without mutual interaction
Argon	$7.3 \times 10^{14}$	0.87	$6.7 \times 10^7$	$4.7 \times 10^7$
Krypton	7.4	1.18	7.4	5.1
Xenon	5.9	1.39	8.0	4.6

packing is given in table II.

The electric field  $E$  is given by the equation for the moment of an induced dipole

$$p = \alpha E \quad (13)$$

where  $\alpha$  is the polarizability of the particle in cubic centimeters (Leigh Page, ref. 21, p. 382). Equations (1), (8), and (13) combine to give

$$E_0 = \frac{-\Delta\phi}{4\pi\sigma_m} \left( \frac{1}{\alpha} + \beta\sigma_m^{3/2} \right) \quad (14)$$

upon setting  $\overline{\cos \theta} = 1$  so that  $p = p_n$ .

The values of  $E_0$  computed from the data of table II by means of equation (14) are shown in table III. The electric field including mutual interaction represents the use of equation (14) with  $\beta\sigma_m^{3/2}$  incorporated. The electric field without mutual interaction omits this term. The value of  $E_0$  computed for tungsten is seen to depend upon the particular rare gas adsorbed. In addition these values are about twice as large as the ones shown in table I, when mutual interaction is included.

Adsorption of rare gases on graphite. - The foregoing values of  $E_0$  for tungsten and molybdenum can be compared to a value computed by Gundry and Tompkins (ref. 22) for a graphite surface from observations of inert gas adsorption. They assumed that the binding energy of rare gases on graphite was represented by two terms. One,  $Q_d$ , corresponded to the dispersion or Van der Waal's forces; the other,  $Q_c$ , represented the effect of polarization in the surface electric field. The magnitude of  $Q_c$  was found by subtracting  $Q_d$  from

experimental heats of adsorption. The electric field was then found from the relation

$$Q_c = - \frac{1}{2} \alpha E^2$$

the mean value for neon (Ne), Ar, Kr, and Xe being  $1.27 \times 10^8$  volts per centimeter. Then from the equation for moment of an induced dipole (eq. (13)) and from equation (1) the change in work function  $\Delta\phi$  was computed for the inert gases on graphite. These  $\Delta\phi$  were larger than those measured on tungsten. By a 10 percent adjustment in one of the assumed parameters, Gundry and Tompkins brought the computed  $\Delta\phi$  for graphite into better line with those obtained for rare gases on tungsten (Ehrlich and Hudda, ref. 18, and Gomer, ref. 19). In addition, this adjustment gave an  $E_0$  for graphite of  $4 \times 10^7$  volts per centimeter ( $1.34 \times 10^5$  stat V/cm). Again, this latter value of  $E_0$  compares very favorably with those in tables I and II, although it is for a different adsorbent. The computations of Gundry and Tompkins apparently do not include the depolarizing effect due to the electric field of the adsorbate atom dipoles.

#### Question of Dipole Images

In the studies of Dykman (ref. 12) the image of the erected permanent dipole in the metal surface was neglected in computing the attenuation of the surface electric field according to equation (8). This practice was followed in the analysis herein of the CsF data of Aamodt, et al. (ref. 7) involving permanent dipoles, and in the analysis of the data of Ehrlich and Hudda (ref. 18) involving induced dipoles. In a theoretical study of work function change in monolayer adsorption, MacDonald and Barlow (ref. 23) also omitted the contribution of images of induced and permanent dipoles to the surface electric field, stating that dipole imaging is almost invariably neglected. They refer to such a treatment as an approximation, implying that a more detailed study would include the image effects.

Some workers (Culver and Tompkins, ref. 24) have questioned the reality of image charges altogether. Others (Sachs and Dexter, ref. 25) have pointed out that the classical image force theory must be corrected for charges of the magnitude  $e$  when the surface is approached to within atomic dimensions.

It appears from the foregoing that the question of whether to include or omit the image dipole for the present case of the erected dipole cannot be resolved with the information available at present. In the absence of further information it seems as justifiable to omit it as to include it. For the cesium-fluorine data of Aamodt, et al. (ref. 7), inclusion of the image dipole increases the computed strength of the surface electric field about 66 percent.

#### CONCLUDING REMARKS

The study herein, prompted by interest in thermionic converters containing multiple additives (both electronegative and electropositive atoms), has been

concerned with the structure of the adsorbate layer on the surfaces. The erected dipole model, in which polar molecules are erected by a strong surface electric field, was discussed. Evidence for this structure, deduced by other authors from data for BaO and CsCl on W, was reviewed.

Data for the system Cs on fluorinated molybdenum were analyzed herein with the aid of a modified version of the erected dipole model using the known dipole moment of gaseous CsF. The computed surface electric field of about  $3.5 \times 10^7$  volts per centimeter agrees well with that calculated for the BaO-W and CsCl-W systems, giving further support to the erected dipole model. The electric fields causing erection of BaO, CsCl, and CsF are within a factor of about 2 of the field believed to cause polarization of rare gas atoms on tungsten. It was demonstrated that as surface temperature is raised at constant dipole coverage, work function must also increase in the erected dipole configuration.

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, September 28, 1965.



## APPENDIX A

### SYMBOLS

A	preexponential in Arrhenius rate equation
E	magnitude of surface electric field, stat V/cm or V/cm
$\vec{E}$	surface electric field, stat V/cm or V/cm
e	charge on electron
G	fraction of cesium atoms arriving at surface that adsorb
k	Boltzmann constant, $1.3803 \times 10^{-16}$ erg/ $^{\circ}$ K
$k$	specific desorption rate
L	Langevin function defined by eq. (6)
p	magnitude of moment of electric dipole, (stat C)(cm) or debye
$Q_c$	adsorption energy due to polarization
$Q_d$	adsorption energy due to dispersion forces
R	gas constant, 1.9872 cal/(mole)( $^{\circ}$ K)
r	magnitude of radius vector between two adsorbed particles
T	temperature of filament or surface, $^{\circ}$ K
$T_R$	cesium reservoir temperature, $^{\circ}$ C
U	energy of dipole in electric field, ergs
W	adsorption or desorption rate, particles/(cm <sup>2</sup> )(sec)
$\alpha$	polarizability of particle, cm <sup>3</sup>
$\beta$	Topping constant, $\sim 9$
$\eta$	independent variable in definition of Langevin function (eq. (6)) defined by eq. (7) for dipoles oriented by electric field
$\theta$	angle between adsorbed dipole and surface normal
$\vec{i}$	unit vector
$\mu_a$	arrival rate of cesium atoms at surface irrespective of whether adsorption occurs

$\sigma$  surface density, particles/cm<sup>2</sup>  
 $\phi$  work function, stat V or V  
 $\Delta\phi$  work function difference,  $\phi - \phi_0$ , stat V or V  
 $\chi$  activation energy for desorption, cal/mole

Subscripts:

$a$  arriving (at surface)  
 $d$  departing (from surface)  
 $f$  pertaining to free sites  
 $i, j$  oscillating dipoles of single species  
 $k$  nonoscillating dipoles of single species  
 $m$  monolayer  
 $n$  normal to surface  
 $s$  adsorption site  
 $t$  tangential to surface  
 $0$  pertaining to bare surface  
 $1$  oscillating dipole (CsF herein)  
 $3$  nonoscillating dipole (F herein)

## APPENDIX B

### MEAN ANGLE OF ERECTED DIPOLE WITH SURFACE

#### NORMAL FOR TWO ADSORBED SPECIES

The equation derived by Dykman (ref. 12) for  $\overline{\cos \theta}$  assumed the presence on the surface of oscillating dipoles only (no English translation has been published). In the event that another species is present having dipoles that do not oscillate, the derivation of Dykman can be modified accordingly. Included here is a brief derivation for this situation which follows loosely that of Dykman and from which his equations can be found.

It is convenient at the outset to define unit vector  $\vec{t}_n$  normal to, and  $\vec{t}_t$  tangential to, the surface (see fig. 6). The oscillating dipole of species 1 will bear indexes  $i, j$ . The nonoscillating dipole of species 3 will bear indexes  $k$ .

The energy  $U_i$  of an oscillating rigid dipole  $i$  in the surface electric field  $\vec{E}_i$  at the location of  $i$  is (ref. 21, p. 381)

$$\vec{U}_i = -\vec{p}_i \cdot \vec{E}_i \quad (B1)$$

where  $\vec{p}_i$ , the dipole moment vector, is given by

$$\vec{p}_i = p_i (\vec{t}_n \cos \theta_i + \vec{t}_t \sin \theta_i) \quad (B2)$$

Moreover,

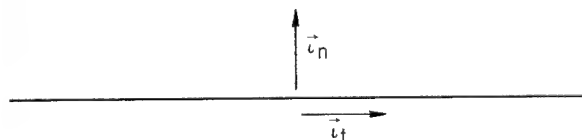
$$\vec{E}_i = \vec{E}_0 + \vec{E}_{i1} + \vec{E}_{i3} \quad (B3)$$

where

$\vec{E}_0$  permanent surface electric field at  $i$

$\vec{E}_{i1}$  contribution of all other oscillating dipoles, species 1, to electric field at  $i$

$\vec{E}_{i3}$  contribution of all nonoscillating dipoles, species 3, to electric field at  $i$



Assume that the distance of charge separation in all dipoles is small compared to the distance between their centers. Then by reference 21 (pp. 380-381)

Figure 6. - Orientation of unit vectors at surface.

$$\vec{E}_{i1} = \sum_{\substack{j=1 \\ j \neq i}}^{\infty} \frac{p_1}{r_{ij}^3} \left( -\vec{t}_n \cos \theta_j + 2\vec{t}_t \sin \theta_j \right) \quad (B4)$$

where  $r_{ij}$  is distance from dipole  $i$ , species  $1$ , to another dipole of same species. By virtue of the fact that the nonoscillating dipoles are normal to the surface

$$\vec{E}_{i3} = - \sum_{k=1}^{\infty} \frac{p_3}{r_{ik}^3} \vec{t}_n \quad (B5)$$

where  $r_{ik}$  is the distance from dipole  $i$ , species  $1$ , to dipole  $k$  of species  $3$ . The permanent surface electric field has been assumed normal to the surface; hence,

$$\vec{E}_0 = E_0 \vec{t}_n \quad (B6)$$

Concerning equation (B4), it is assumed that in the mean there is no correlation between  $\theta_j$  and  $r_{ij}$ . Replace  $\cos \theta_j$  by its mean,  $\overline{\cos \theta}$ , the mean value of the cosine for all erected dipoles, in equation (B4). In the mean, no tangential component of electric field is to be expected in the idealized model here, implying that the contribution of  $2\vec{t}_t \sin \theta_j$  vanishes. Equation (B3) then gives

$$\vec{E}_i = \left( E_0 - p_1 \overline{\cos \theta} \sum_{\substack{j=1 \\ j \neq i}}^{\infty} \frac{1}{r_{ij}^3} - p_3 \sum_{k=1}^{\infty} \frac{1}{r_{ik}^3} \right) \vec{t}_n \quad (B7)$$

If the adsorbed particles lie in a regular plane array, the summations can be expressed in terms of the dipole densities, times a constant factor. Topping (ref. 26) showed that for a regular plane array, the summations of equation (B7) can be written

$$\sum_{\substack{j=1 \\ j \neq i}}^{\infty} \frac{1}{r_{ij}^3} = \beta \sigma_1^{3/2} \quad \text{and} \quad \sum_{k=1}^{\infty} \frac{1}{r_{ik}^3} = \beta \sigma_3^{3/2} \quad (B8)$$

where

$\sigma$  density of points in array

$\beta$  9.034 for square array

$\beta$  8.893 for equitriangular array

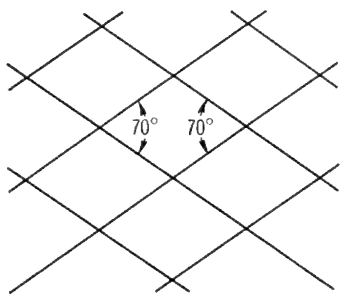


Figure 7. - Geometry of (100) plane of body-centered cubic crystal.

For an array having the geometry of the (110) plane of a body-centered cubic crystal (see fig. 7),  $\beta$  was evaluated by the method of Topping for the present report. The value was found to be  $\beta = 8.941$ . A value for  $\beta$  of 9 suffices for these situations.

If the adatoms are immobilized on an underlying lattice of adsorption sites, then a regular array can be achieved theoretically only for certain fractional coverages (Moore and Allison, ref. 2). It is customary, however, to regard equation (B8) as holding approximately for all coverages. It will be assumed that equation (B8) applies to the summations in equation (B7) so that

$$\vec{E} = \vec{t}_n E$$

where

$$E = E_0 - \beta p_1 \sigma_1^{3/2} \overline{\cos \theta} - \beta p_3 \sigma_3^{3/2} \quad (B9)$$

Substituting equations (B2) and (B9) into equation (B1) gives

$$U_i = -p_i E \cos \theta_i \quad (B10)$$

The mean value,  $\overline{\cos \theta}$ , is defined classically as

$$\overline{\cos \theta} = \frac{\int_0^\pi \cos \theta \sin \theta d\theta \exp\left(\frac{p_1 E \cos \theta}{kT}\right)}{\int_0^\pi \sin \theta d\theta \exp\left(\frac{p_1 E \cos \theta}{kT}\right)} \quad (B11)$$

(ref. 15, p. 329). Upon performing the integration, it is found that

$$\overline{\cos \theta} = L(\eta) \quad (B12)$$

where

$$L(\eta) = \coth \eta - \frac{1}{\eta} \quad (B13)$$

which is the Langevin function, and

$$\eta = \frac{p_1 E}{kT} \quad (B14)$$

with  $E$  given by equation (B9). Equations (B12) to (B14), pertaining to the adsorption of both oscillating and nonoscillating dipoles, turn out to be the same as equations (5) to (7) for oscillating dipoles only.

The equations of Dykman (ref. 12) are obtained by setting  $\sigma_3$  equal to zero in equation (B9).

## APPENDIX C

### ANALYSIS OF CESIUM FLUORIDE ADSORPTION DATA

The equation for work function difference with both the erected CsF molecules and fluorine atoms present is

$$\Delta\phi = -4\pi\sigma_1 p_L L(\eta) - 4\pi p_3 \sigma_3 \quad (C1)$$

The minimum work function of a run such as run 6 of figure 4 (p. 7) at a cesium reservoir temperature of 68° C is described by

$$\left( \frac{\partial \phi}{\partial \ln \sigma_1} \right)_{T_R} = 0 \quad (C2)$$

Equations (C1) and (C2) are to be solved for cesium fluoride coverage  $\sigma_1$  at the minimum work function, and for surface electric field strength  $E_0$ . An expression for equation (C2) can be derived as follows:

Figure 4 gives a relation between  $T_R$ ,  $\phi$ , and  $T$  where  $T_R$  is cesium reservoir temperature and  $T$  is filament or emitter temperature

$$T = T(\phi, T_R) \quad (C3)$$

By the surface phase postulate of Taylor and Langmuir (ref. 1), all the properties of an adsorbed phase on a substrate of given composition are uniquely determined by coverage and surface temperature. Therefore, for figure 4,  $\phi$  is a function of  $\sigma_1$ ,  $\sigma_3$ , and  $T$ ; that is,

$$\phi = \phi(\sigma_1, \sigma_3, T) \quad (C4)$$

For any run of figure 4 the cesium is presumed to be adsorbed on a monolayer coverage  $\sigma_{3m}$  of fluorine to form CsF. The case of fractional coverages of fluorine was not considered. Thus,

$$\sigma_3 = \sigma_{3m} - \sigma_1 \quad (C5)$$

and by equations (C3), (C4), and (C5)

$$\phi = \phi(\sigma_1, T_R) \quad (C6)$$

Also by equations (C3), (C4), and (C5)

$$T = T(\sigma_1, T_R) \quad (C7)$$

By equations (B9), (B12), (B13), (B14), and (C5) it can be seen that  $L(\eta)$  is also a function of  $\sigma_1$  and  $T$  alone

$$L = L(\sigma_1, T) \quad (C8)$$

From equations (C1), (C5), and  $\Delta\varphi = \varphi - \varphi_0$ ,

$$d\varphi = -4\pi\sigma_1 \left[ p_1 L (d \ln L + d \ln \sigma_1) - p_3 d \ln \sigma_1 \right] \quad (C9)$$

By equation (C8)

$$d \ln L = \left( \frac{\partial \ln L}{\partial \ln \sigma_1} \right)_T d \ln \sigma_1 + \left( \frac{\partial \ln L}{\partial \frac{1}{T}} \right)_{\sigma_1} d \frac{1}{T} \quad (C10)$$

Combining equations (C2), (C9), and (C10) and taking the derivative with respect to  $\sigma_1$  gives at the minimum work function

$$\begin{aligned} \left( \frac{\partial \varphi}{\partial \ln \sigma_1} \right)_{T_R} &= 0 \\ &= -4\pi\sigma_1 p_1 L \left[ 1 + \left( \frac{\partial \ln L}{\partial \ln \sigma_1} \right)_T + \left( \frac{\partial \ln L}{\partial \frac{1}{T}} \right)_{\sigma_1} \left( \frac{\partial \frac{1}{T}}{\partial \ln \sigma_1} \right)_{T_R} - \frac{p_3}{p_1 L} \right] \end{aligned} \quad (C11)$$

The terms  $p_3/p_1 L$  and

$$\left( \frac{\partial \ln L}{\partial \frac{1}{T}} \right)_{\sigma_1} \left( \frac{\partial \frac{1}{T}}{\partial \ln \sigma_1} \right)_{T_R}$$

can be shown to be considerably smaller than unity, so that equation (C11) is very similar to equation (9), solved by Dykman for BaO and CsCl adsorption.

The derivatives in equation (C11) can be expressed as follows: From equations (B9), (B13), and (B14) it can be shown easily that

$$\left( \frac{\partial \ln L}{\partial \frac{1}{T}} \right)_{\sigma_1} = \frac{T \frac{d \ln L}{d \ln \eta}}{1 + \frac{\beta p_1 \sigma_1^{3/2}}{E} L \frac{d \ln L}{d \ln \eta}} \quad (C12)$$

and

$$\left( \frac{\partial \ln L}{\partial \ln \sigma_1} \right)_T = \frac{-\frac{3}{2} \beta \frac{\sigma_1}{E} \left[ p_1 \sigma_1^{1/2} L - p_3 \sigma_3^{1/2} \right] \frac{d \ln L}{d \ln \eta}}{1 + \frac{\beta p_1 \sigma_1^{3/2}}{E} L \frac{d \ln L}{d \ln \eta}} \quad (C13)$$

where

$$\frac{d \ln L}{d \ln \eta} = - \frac{\eta}{L} \left( \operatorname{csch}^2 \eta - \frac{1}{\eta^2} \right) \quad (C14)$$

On the other hand

$$\left( \frac{\partial \frac{1}{T}}{\partial \ln \sigma_1} \right)_{T_R}$$

presents more difficulty. It will be defined in the following manner.

Figure 4 represents a steady-state condition with respect to arrival and departure of cesium from the fluorinated filament. The adsorption rate  $W_{1a}$  for cesium can be represented as

$$W_{1a} = \mu_a G(\sigma_1) \quad (C15)$$

where

$\mu_a$  arrival rate of cesium at surface determined by  $T_R$ , atoms/(sq cm)(sec)

$G(\sigma_1)$  condensation factor,  $0 < G \leq 1$

See Taylor and Langmuir (ref. 1).

The desorption rate can be expressed as

$$W_{1d} = k_1 \sigma_1 \quad (C16)$$

where  $k_1$  is a temperature and coverage dependent specific desorption rate. It is convenient to assume a simple Arrhenius form for  $k_1$

$$k_1 = A \exp(-X/RT) \quad (C17)$$

where

A constant

X activation energy for desorption, cal/mole

R gas constant 1.9872 cal/(mole)(°K)

Equating equations (C15) and (C16) and using equation (C17) give

$$\mu_a G = A \sigma_1 \exp(-X/RT) \quad (C18)$$



Since  $\mu_a = \mu_a(T_R)$ , differentiation of equation (C18) yields, in view of equation (C5),

$$\left( \frac{\partial \ln \sigma_1}{\partial \frac{1}{T}} \right)_{T_R} = \frac{\frac{\chi}{R}}{-\frac{\sigma_1}{G} \frac{dG}{d\sigma_1} + 1} \quad (C19)$$

An approximate value of  $\chi$  can be obtained from reference 7. The authors have crossplotted the data of their figure 7 (fig. 4 herein) to show  $\mu_a$  as a function of  $1/T$  at constant  $\phi$ . The resulting plot, figure 8 of reference 7, is shown herein as figure 8. By equation (C18)

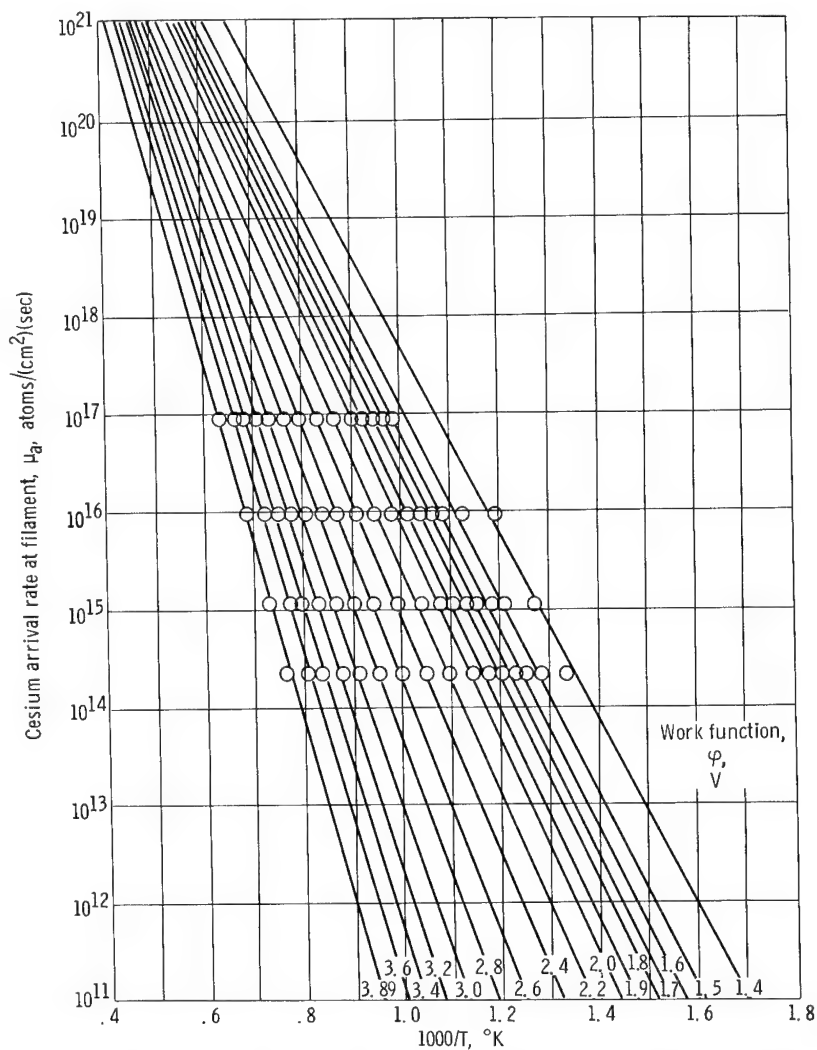


Figure 8. - Equilibrium evaporation (arrival) rate of Cs on fluorine-coated Mo at constant work function, as function of  $1000/T$ . (Data of ref. 7.)

$$\frac{\chi}{R} = - \left( \frac{\partial \ln \mu_a}{\partial \frac{1}{T}} \right)_{\sigma_1} \quad (C20)$$

Assuming as a first approximation that  $\phi$  is a function of  $\sigma_1$  alone, it can be shown that the slopes of the lines of constant  $\phi$  in figure 8 give  $\chi/R$  in equation (C20). A plot of this  $\chi$  against  $\phi$  is shown herein as figure 9. At the minimum work function of around 1.4,  $\chi$  is about 44 000 calories.

Two extremes will be found for the value of the derivative of  $G$ . It will be demonstrated below that the magnitude of  $E_0$  is insensitive to the choice made for this derivative.

In one extreme,  $G$  will be assumed constant and equal to unity, so that  $dG/d\sigma_1$  is zero. This is the situation found by Taylor and Langmuir (ref. 1) in the case of cesium on tungsten alone. It will be designated here as the no-reflection case.

In the other extreme, which will be designated as the free-site case, it will be assumed that a cesium atom impinging on the surface cannot adsorb unless there is a free site available, containing a waiting fluorine atom. The definition of a free site is that of Tonks (ref. 27).

Tonks points out that in adsorption on fixed sites, the adsorbed atom can be so large as to block not only the occupied site, but to cover neighboring sites. Adsorption on a covered site would involve some interference with the

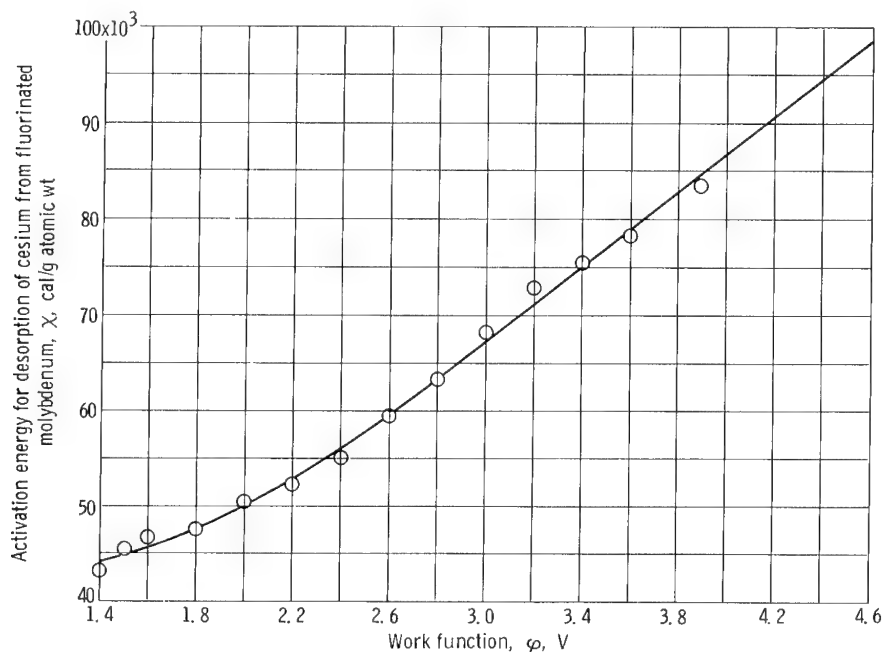


Figure 9. - Activation energy for desorption of cesium from fluorinated molybdenum against work function. Plotted from figure 8.

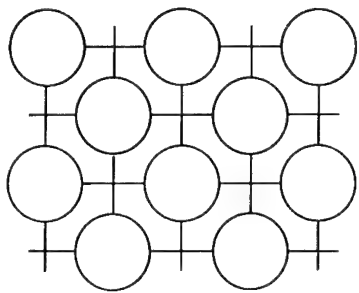


Figure 10. - Monolayer adsorption of cesium on (100) plane of molybdenum.

already adsorbed atom on the occupied site. Only sites both unoccupied and uncovered are designated as free.

A cesium ion has a diameter of about 3.4 angstroms (Pauling, ref. 28, table 13-3, p. 514). The lattice constant of molybdenum is 3.14 angstroms (Kittel, ref. 29, p. 40). This will be the spacing of molybdenum atoms in the (100) plane, which will be assumed here. With closest packing, only one cesium ion can be adsorbed for every two molybdenum atoms, as shown in figure 10 which depicts monolayer adsorption.

Tonks defined a fractional surface coverage of cesium ( $\theta$ ) such that, when the arrangement shown in figure 10 is reached,  $\theta = 1$ . (This is not to be confused with the polar angle  $\theta$ .) For cesium coverages up to 0.5, Tonks found that the following equation represents the fraction of adsorption sites that are free:

$$\theta_f = 1 - \frac{5}{2} \theta + \frac{3}{2} \theta^2 + \frac{3}{4} \theta^3 \quad (C21)$$

In the case herein of cesium adsorption on fluorinated molybdenum, it will be assumed that a monolayer of fluorine contains one fluorine atom for every molybdenum atom. The  $F^-$  ion with a diameter of 2.7 angstroms is smaller than the lattice spacing of the (100) plane of molybdenum and the F atom will be even smaller. Thus,

$$\sigma_{3m} = \sigma_s \quad (C22)$$

where  $\sigma_s$  is the total number of adsorption sites per square centimeter. Equation (C21) will be considered as defining  $G$  for the free-site case of adsorption on fluorinated molybdenum. First, Tonk's  $\theta$  can be redefined in terms of CsF coverage  $\sigma_1$  and adsorption site density  $\sigma_s$ ; thus

$$\theta = 2\sigma_1/\sigma_s$$

Then, from equation (C21)

$$G = 1 - 5 \frac{\sigma_1}{\sigma_s} + 6 \left( \frac{\sigma_1}{\sigma_s} \right)^2 + 6 \left( \frac{\sigma_1}{\sigma_s} \right)^3 \quad (C23)$$

valid to  $\sigma_1/\sigma_s = 0.25$ . From this for the free-site case,

$$\frac{dG}{d\sigma_1} = \frac{1}{\sigma_s} \left[ -5 + 12 \left( \frac{\sigma_1}{\sigma_s} \right) + 18 \left( \frac{\sigma_1}{\sigma_s} \right)^2 \right] \quad (C24)$$

A choice for  $p_3$  remains to be made. The (100) plane which has been assumed herein has a surface atom density of  $1.01 \times 10^{15}$  molybdenum atoms per square centimeter. By equation (C22) this is also the density of a fluorine monolayer. Aamodt, et al. (ref. 7) coated molybdenum with fluorine to an extent that will be considered here to be a monolayer and obtained a work function difference of 0.6 volt. From this information, equation (1) gives a value for adsorbed fluorine atom dipole moment  $p_3$  of about -0.16 debye.

With equations (C12), (C13), (C14), (C19), and the chosen values of  $\chi$ ,  $p_1$ , and  $p_3$  in hand, equations (C1) and (C11) can be solved for  $E_0$  from conditions at the minimum work function of run 6, figure 4. For the no-reflection case  $E_0$  turns out to be  $1.18 \times 10^5$  stat volts per centimeter or  $3.54 \times 10^7$  volts per centimeter, and  $\sigma_1$  is  $1.922 \times 10^{14}$  CsF molecules per square centimeter. For the free-site assumption  $E_0$  again is  $1.18 \times 10^5$  stat volts per centimeter or  $3.54 \times 10^7$  volts per centimeter, with a  $\sigma_1$  of  $1.934 \times 10^{14}$  CsF molecules per square centimeter. The electric field strength apparently experiences compensating effects which make it insensitive to these assumptions, while the coverage  $\sigma_1$  changes slightly.

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